The Pennsylvania State University

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(DOE-NEER Project)

Report for Phase 2
Study of Second Phase Particles and Fe content in Zr Alloys Using the Advanced Photon Source at Argonne

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Overall Project Goal – The aim of this project is to investigate the state of alloying elements and second phase particles in Zr alloys using synchrotron radiation from the Advanced Photon Source (APS) at Argonne National Laboratory. Several zirconium alloys have been investigated with the aim of determining both the volume fraction and crystal structure of minute amounts of second phase precipitate particles using x-ray diffraction and the alloying content in the zirconium matrix using μbeam x-ray fluorescence.

The objectives for phase 2 in last year's report, are listed below:

1. To obtain reliable values for the Fe concentration in the hcp-Zr matrix of non-irradiated Zr alloys using the microbeam facilities at APS; the alloys to be studied include ultra purity Zr, Zircaloy-2, Zircaloy 4 and ZIRLO. We will study the influence of heat treatment on Fe content in the matrix as well as the Fe spatial distribution.

2. To demonstrate our ability to detect and identify the various second phase precipitates in Zircaloys and ZIRLO, also as a function of heat treatment.

Both of these objectives have been accomplished and surpassed. For objective number 1, not only these alloys but others were studied, using the microfluorescence beams at the 2-IDE beamline at Argonne. We have also performed Monte Carlo simulations of the fluorescence process and can therefore reproduce and predict the fluorescence spectra we measure. For objective number 2, we have studied both Zircaloy-2 and Zircaloy-4 and ZIRLO, in various states of heat treatment, from as-quenched to highly annealed. We have not only verified that the precipitates can be detected and identified but also verified that one can observe the kinetics of precipitate nucleation and growth using synchrotron radiation. We are now performing Rietveld analysis of the data to quantify the precipitates volume fraction. Two conference papers and one journal submission have so far resulted, as well as a completed M.Sc. thesis.

1. Introduction

During this funding period, we achieved several goals, in both areas of the project. We have conducted several runs in the diffraction line at APS to obtain data that will allow us to evaluate the volume fraction of second-phase precipitates in zirconium alloys as a function of heat treatment. To our knowledge these observations represented the first time that such minute amounts of second phase particles were detected using a bulk diffraction technique. They are the subject of one conference publication and a recent journal submission [1, 2]. We have also started to perform quantitative analysis of the diffraction spectra using the Rietveld method [3]. When this analysis is achieved, we will have a method to quantitatively analyze the amount of second phase particles in zirconium alloys, as a function of processing route and irradiation conditions. This will allow much more detailed modeling and prediction of alloy behavior.

We have also conducted detailed examinations of the matrix of several alloys and standards in the micro-fluorescence line at APS, with the aim of detecting the amount of alloying elements in the alpha-matrix of zirconium alloys. We have analyzed various alloys and fabricated standards with a homogeneous distribution of alloying elements, with results that fit well with existing knowledge. We have also conducted preliminary examinations using microbeam fluorescence in alloys with a heterogeneous distribution of alloying elements (second phase intermetallic precipitates in a zirconium matrix) and found results that are also in agreement with our analysis. The initial analyses have been the subject of one conference presentation [4]. A run that is planned for August in the highest resolution microbeam line will allow us to determine the alloying content in the matrix of zirconium alloys. To analyze these results we have been performing Monte Carlo simulations of the fluorescence process [5, 6] to analyze our initial results and to predict the outcome of the high-resolution experiment to be conducted in August.

The detailed report from the two areas follows, as well as a small section on the status of the neutron-irradiated samples. The research project is going very well, producing new information and revealing the potential of a new technique to analyze the microstructure of zirconium alloys.

2. Bulk diffraction studies (students: Ken Erwin and Olivier Delaire, Collaborators: Y.Chu, D.Mancini (SRI-CAT, ANL), R.Birtcher (MSD-ANL))

We have performed several examinations of zirconium alloys and especially prepared standards in the 2BM (bending magnet line at the SRI-CAT at Argonne in the current funding period. These examinations, aided by complementary experiments in the TEM and by computer analysis of the diffraction patterns using GSAS, have demonstrated that this technique can provide a measure of the precipitate volume fraction in these alloys, and that precipitation of second phases can be detected at very small values of the annealing parameter (CAP) and followed quantitatively as a function of heat treatment.

This work forms the basis of the recently completed M.Sc. thesis by K.T.Erwin [7], and of a recently submitted article to Journal of Nuclear Materials and of others currently in preparation.

During the funding period we performed three experimental runs at APS, on 8/99, 2/00 and 5/00. The three experiments are summarized in table 1, with beam conditions, samples examined and objectives. A significant fraction of our travel budget was spent on those trips. The detailed results we obtained are summarized in the following sections.

2.1 Identification of precipitate crystal structures

Figure 1 shows the diffracted intensities as a function of two-theta angle for a two theta scan of Zircaloy-4 sheet, annealed to CAP=10^{-16} h. The x-ray peak locations correspond well with those reported for alpha-Zr and for the hexagonal C14 $Zr(Fe_{1.5}Cr_{0.5})_2$ Laves phase (Joint Committee for Powder Diffraction File # 42-1289). These are the stable second-phase intermetallic compound precipitates in Zircaloy-4.

It is noteworthy that these small amounts of precipitates can be detected in the bulk material. Chemical analysis of the alloys studied here (table 1) shows that the Cr+Fe concentration is 0.35% in Zircaloy-4. We can calculate an upper bound of the total precipitate volume fraction of 0.46%. If the alloying elements are not completely precipitated, this volume fraction would be lower. This range of second phase volume fractions are very difficult to detect in the bulk and to our knowledge, this is the first time that such small precipitate volume fractions have been detected by bulk diffraction.

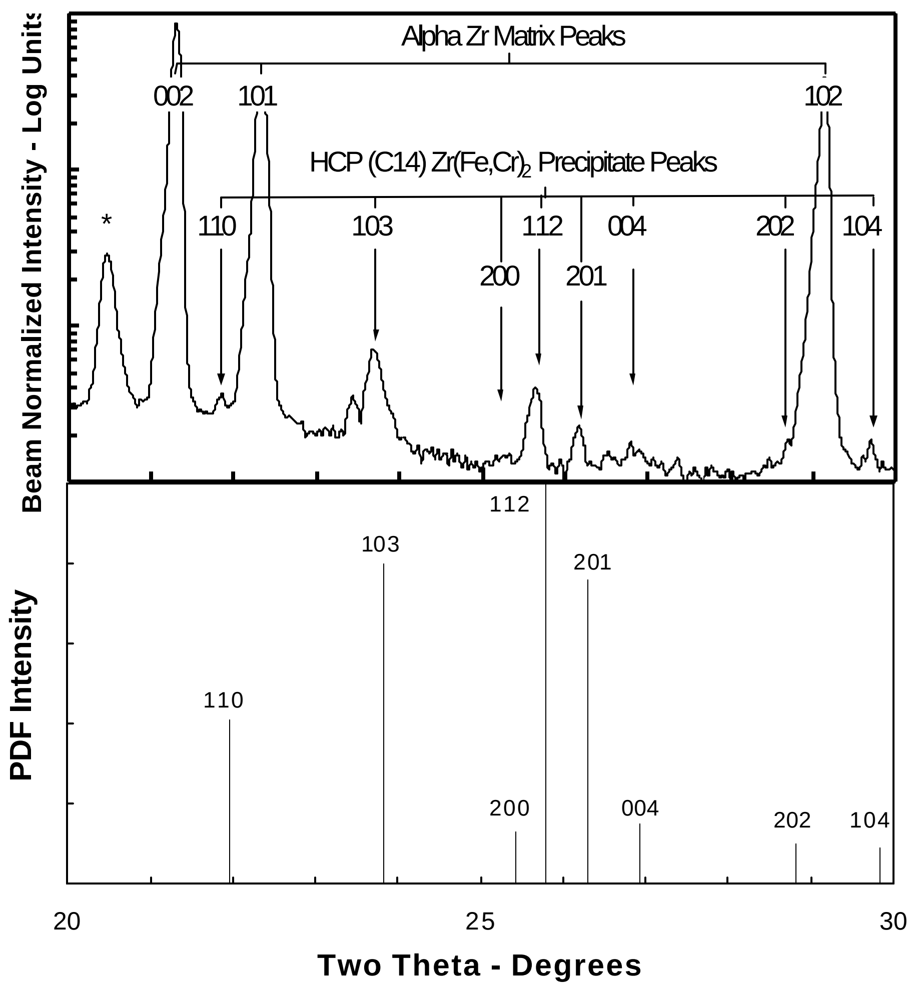

Figure 1: Two-theta X-ray diffraction pattern for Zircaloy-4 obtained with synchrotron radiation at APS, and reported powder diffraction file intensity for $Zr(Fe_{1.5}Cr_{0.5})_2$ (Joint Committee for Powder Diffraction File # 42-1289) (asterisks indicate unindexed peaks).

2.2 Precipitation Kinetics

Figure 2 shows the result of x-ray diffraction scans analogous to the above, but performed on a series of Zircaloy-4 samples that were quenched and annealed to a range of annealing parameters between 7.8 x 10^{-21} h (quenched state) and 10^{-16} h. The intermetallic precipitates grow upon annealing heat treatment following quench from the beta-phase, so that longer CAPs result in larger precipitate particles. These results indicate that we can follow the second-phase precipitation kinetics using x-ray diffraction.

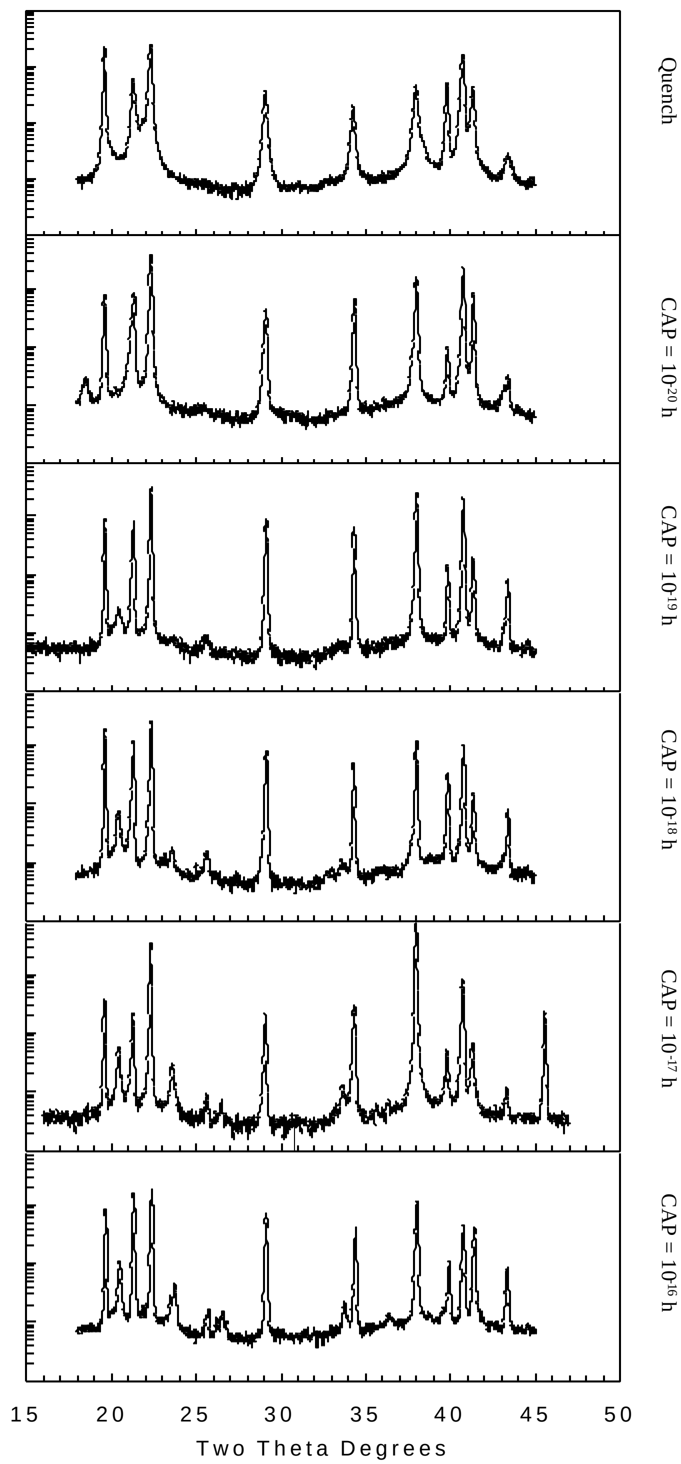

Figure 2: Series of two-theta x-ray diffraction scans of Zircaloy-4 obtained on a series of samples with increasing cumulative annealing parameter (CAP).

2.3 Quantification of precipitate volume fraction

We have started to quantify the precipitate volume fraction using Rietveld analysis. The basic principle behind the Rietveld method is to refine the least squares fitting of the diffraction profile by systematically varying the various parameters that affect x-ray diffraction intensities. The computer adjusts physical parameters in the system and attempts to minimize the difference between the refined theoretical pattern and the data obtained. Currently, there are several computer programs used to perform Rietveld analysis. The program used in this research, GSAS [3], is maintained at Los Alamos National Laboratory and consists of a set of programs for the processing and analysis of both single crystal and powder diffraction data obtained with x-rays or neutrons. We attended a workshop to learn the GSAS method in Washington (5/00) and have been using the program to fit our data. We are currently working on improving the absolute fit of the diffraction patterns obtained, so that a direct quantification of the precipitate volume fraction can be derived from the data.

3. Microbeam Fluorescence Study of Precipitates in Zircaloy (students: O.Delaire, A.Yilamzbayhan, and K.T.Erwin; Collaborators: J.Maser, B.Lai (SRI-CAT, ANL) and R.C.Birtcher, (MSD-ANL))

Using the x-ray micro-focusing beam line at the APS devised by Yun et al.[8], we have been studying the concentrations of alloying elements such as Fe in the matrix of zirconium alloys. The apparatus creates a micro-beam with a diameter as small as 0.1 μm in diameter. This is a unique capability of this beam line, which allows us to obtain detailed structural information with very high spatial resolution.

3.1 X-ray Fluorescence Study of alloying element content in zirconium alloys.

The alloying element content present in the α-Zr matrix of Zr alloys, especially the concentration of transition elements Fe, Cr, Ni is crucial to determining the alloy corrosion behavior. However, the levels of these elements are so low that they cannot be measured by traditional measurement techniques such as EDX on the TEM. There are chemical and spectroscopic techniques that can measure very low levels of alloying elements, in the bulk, but these are not suited to determining the alloying element content in specific regions in the microstructure. The unique combination of spatial and elemental resolution needed to measure to study the alloying elements in the hcp matrix of Zr alloys can be achieved at the microbeam line at APS. The objective of this research program is to use the microbeam line at APS to measure the concentrations of alloying elements in the Zr alloy matrix using x-ray fluorescence. The intent is to study these quantities as a function of alloy type, irradiation conditions. The information thus obtained will allow more precise and mechanistic predictions of alloy behavior, especially in conditions of high fuel burnup.

In the runs conducted during this funding period, we examined a series of TEM samples of Zircaloy 4 Zircaloy 2 and ZIRLO, both in the as-fabricated state (which produces the precipitates and low alloying element content in the matrix) and in the quenched state (which produces a homogeneous alloying element distribution equal to the overall alloying element content in the material).

Homogeneous (precipitate-free) alloys: We examined the difference between alloying contents of quenched samples of the different alloys. In this case the beam size does not matter as much since the whole sample is homogeneous, and the values we obtained were in excellent agreement with the nominal values for Zircaloy 4 and the measured values for ZIRLO. We also examined other standards, including nominally pure Zr, and ultra-pure (Fe-free) Zr obtained from AECL, finding that the ratios of concentrations of those standards to the alloys were in good agreement with nominal values, and with independent measurements of the concentration by hot vacuum extraction [9].

Heterogeneous (precipitate-containing) alloys: We have also examined the as-fabricated Zircaloy 4 and the measured alloying content in the matrix was found to be higher than expected, likely as a result of our inability to reduce beam size in the 2ID-E beam line (0.3 x 0.5 μm beam). This should improve once we use the higher resolution 2ID-D beamline (0.1 x 0.2 μm beam). The measurements of the matrix contents in non-homogeneous alloys involves the positioning of the beam "in-between" precipitates to obtain a true matrix sampling count (i.e. a fluorescence spectrum counted for long time, and with the beam located on the matrix). This involves a great deal of positioning the beam using 2D-scans, to find the region in-between precipitates. It also involves detailed geometrical corrections to keep the beam within the depth of focus, so that the beam size is kept close to the values obtained during alignment.

A fair amount of analysis will be required to derive actual concentration numbers from the data, but we believe we have all that is needed to do so. Preliminary evaluations of the data appear to make sense from what we know of the alloys. We also found that the background was quite low, (on the order of 10 counts), which should allow us to perform a good quantitative analysis. During the course of the experiment we uncovered many potential scientific issues that will have to be analyzed and accounted for in the calculations. The main issue is the resolution of the beam, and we expect that in the next experiment in the higher resolution beamline (2ID-D) we will be able to measure the matrix content of the alloys with accuracy.

3.2. Monte Carlo Simulation of Fluorescence Spectra

During the last funding period, we have used the computer program MSIM5D [5, 6] to predict and analyze fluorescence spectra obtained at the synchrotron facility; students have worked extensively on the program and can now use it to help set up and analyze fluorescence experiments. An example of one of these simulations is shown in Figure 3 in which the total number of counts obtained from a fluorescence acquisition from the matrix of Zircaloy-4 is plotted against photon energy. The program fits extremely well the fluorescence peaks across the energy range examined, including the Fe and Cr K_α peaks, as well as the Sn and Zr L peaks. This demonstrates that we can analyze and predict the data obtained with synchrotron radiation at APS.

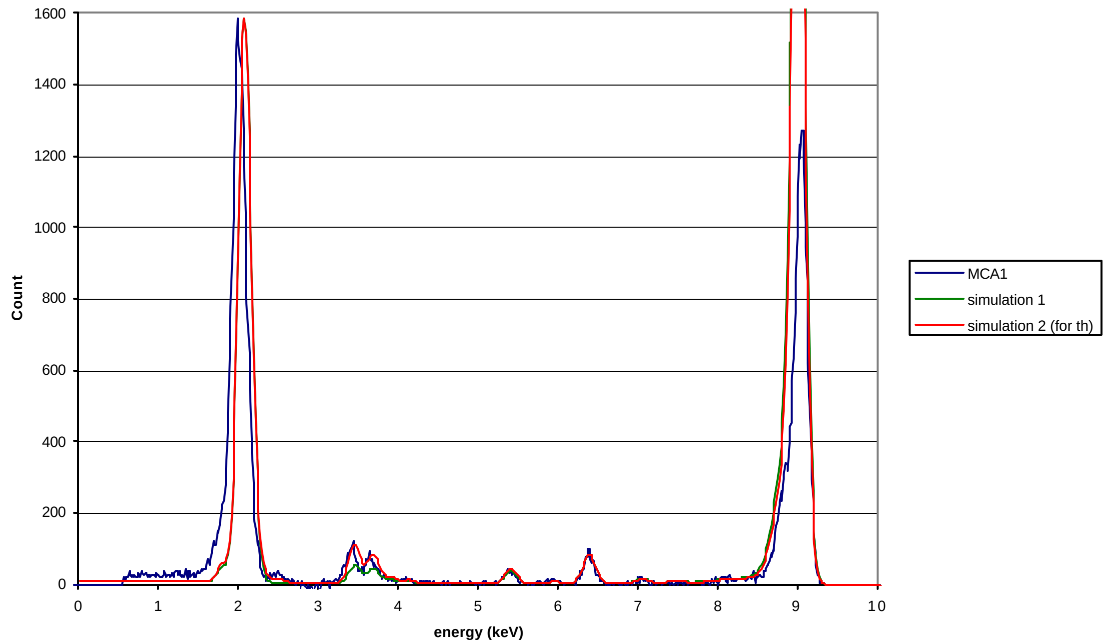

Figure 3: Fluorescence spectrum acquired in the 2-ID-E line at the Advanced Photon Source. Also shown are the fits calculated by the Monte Carlo simulation program.

4. Neutron Irradiated Zircaloy-4 Samples

We have been in contact with Bettis Laboratory to obtain neutron-irradiated Zircaloy TEM samples to perform studies similar to those in parts 2 and 3 above. A proposal was sent to Bettis, to store and study the samples at Argonne, and we are currently awaiting the final details to be arranged for the contract to be in place so that the shipment of the samples can be arranged. The set of samples to be examined include non-irradiated, low medium and high fluence samples. We will examine these as soon as they can be shipped to Argonne, and prepared for examination.

References:

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